

IONIC CONDUCTIVITY OF THE $\text{Na}_2\text{SO}_4\text{-Na}_2\text{WO}_4$ SYSTEM

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ABSTRACT

In this study, the electrical conductivity of the $\text{Na}_2\text{SO}_4\text{-Na}_2\text{WO}_4$ systems has been measured using complex impedance technique to investigate the effect of anion substitution on the cationic conductivity. In the $\text{Na}_2\text{SO}_4(l)$ based solid solubility region the conductivity increases as SO_4^{2-} ions are substituted by WO_4^{2-} in the crystal structure. Maximum Conductivity of $4 \times 10^{-4} \text{ Scm}^{-1}$ with an activation energy 0.5 eV at 450 °C has been observed around 22 mol% Na_2WO_4 . The secondary conductivity maximum observed at 48 mol% Na_2WO_4 could be associated with a two-phase mixture consisting of Na_2SO_4 based and Na_2WO_4 based solid solutions.

1. INTRODUCTION

The high temperature hexagonal phase of Na_2SO_4 , denoted by $\text{Na}_2\text{SO}_4(I)$, can be used as a base material to study the trends in ionic conductivities of Na_2SO_4 type inorganic crystalline materials. Because of the disorder of the positions of oxygen atoms in sulphate tetrahedra in $\text{Na}_2\text{SO}_4(I)$, no individual Na coordination polyhedra can be defined¹. This state of local cations coordination in $\text{Na}_2\text{SO}_4(I)$ appears to favour a large number of cation and anion substitutions².

The migration of Na^+ ions through cation Frenkel defects is predominant in the ionic conductivity mechanism in pure $\text{Na}_2\text{SO}_4(I)$. Therefore, any process tending to increase the point defect concentration may result an increase of conductivity. This fact has been tested in number of studies by substituting many divalent and trivalent cations to increase vacancy concentration and a conductivity enhancement has been observed²⁻⁵. Homovalent Li^+ and Ag^+ substitutions have also resulted a small conductivity increment but in that case the substituted ions were also mobile⁶. Conductivity enhancement by anion substitution has also been reported^{2,7-8}. In an attempt to stabilize the high temperature $\text{Na}_2\text{SO}_4(I)$ phase at room temperature by quenching, Leblanc et al and Prakash et al have studied the conductivity of the binary system. Neither group was able to confirm the identity of the phases present. Also, their conductivity measurements were done only at a fixed frequency of 1kHz. Samples made by slow cooling the melt gives equilibrium phases. Therefore, in the present work, the samples made by this method have been used to study the ionic conductivity of the binary system.

2. EXPERIMENTAL

Anhydrous Na_2SO_4 of purity 99.5% (BDH, England) and analytical reagent Na_2WO_4 of purity 99% (Johnson Mathey, England) were used as starting materials for making different compositions. For the conductivity measurement of pure Na_2SO_4 , anhydrous Na_2SO_4 of purity 99.5% (Grade 1, Johnson Mathey, England) was used. Chemicals were dried at 300 °C for two days prior to making different compositions. Samples were kept in the molten state at 900 °C for one hour and allowed to cool in the furnace. Subsequently each sample was mechanically ground into a fine powder using an agate mortar. Pellets of 13 mm diameter and 1-2 mm thickness were pressed using 20 kN pressure, sintered at 500 °C for 12 hours, and cooled inside the furnace. Gold paste was applied on both flat surfaces of the pellet and kept at 600 °C for 30 minutes to remove the solvent.

Four pellets were simultaneously loaded into a specially designed sample holder and the temperature of the pellet assembly was increased from 200 °C to 575 °C during the measurement. The ionic conductivity was then measured at 25 °C intervals using a HP 4192A impedance analyzer, connected to a HP 86B microcomputer.

3. RESULTS AND DISCUSSION

Conductivity values were obtained from complex impedance plots in the usual way. A single semicircle was seen in the impedance plane plots, indicative of a bulk response. The impedance data showed clear evidence of blocking electrode response, suggesting that the principal current carriers are Na^+ ions. $\ln(\sigma T)$ vs $1000/T$ plots for pure Na_2SO_4 and for the samples with 10, 15, 20, 25, and 30 mol% Na_2WO_4 are shown in Fig. 1. Similar plots for 30-100 mol% Na_2WO_4 are shown in Fig. 2. The Arrhenius parameters, pre-exponential factors and activation energy values for several compositions are given in Table 1.

Table 1. Conductivity Arrhenius parameters for some compositions in $\text{Na}_2\text{SO}_4 + x$ mol% Na_2WO_4 . E_a is the activation energy and A is the pre-exponential factor in $\sigma = (A/T)\exp(E_a/kT)$.

x	E_a /eV	$\ln A$
0	0.74	8.35
10	0.68	9.15
20	0.50	7.04
40	0.60	8.22
100	1.35	15.2

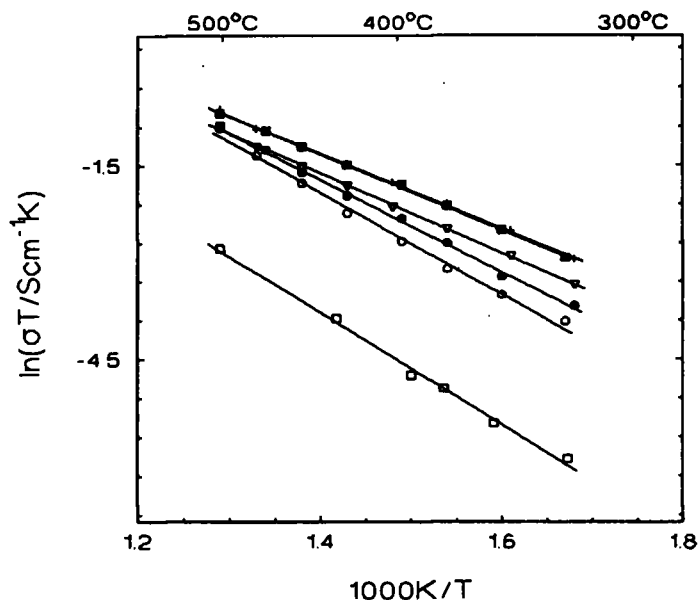


Fig.1 Conductivity Arrhenius plots of pure Na_2SO_4 and of mixtures with upto 30% Na_2WO_4 . (□) pure Na_2SO_4 , (○) 10% Na_2WO_4 , (▽) 15% Na_2WO_4 , (■) 20% Na_2WO_4 , (+) 25% Na_2WO_4 , (●) 30% Na_2WO_4

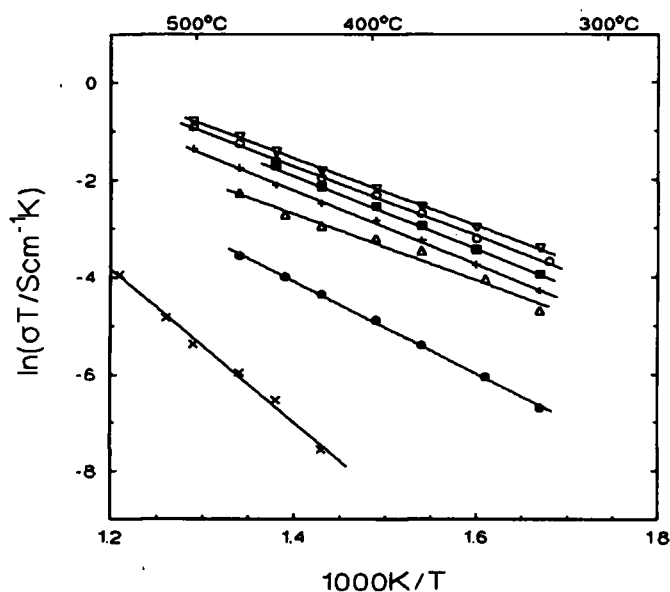


Fig.2 Conductivity Arrhenius plots of Na_2SO_4 with 30, 40, 50, 60, 90 mol% Na_2WO_4 and pure Na_2WO_4 . (○) 30% Na_2WO_4 , (▽) 45% Na_2WO_4 , (●) 50% Na_2WO_4 , (+) 60% Na_2WO_4 , (△) 80% Na_2WO_4 , (●) 90% Na_2WO_4 , (x) pure Na_2WO_4

Variation of conductivity with mole% of Na_2WO_4 is depicted in Fig.3. Na_2SO_4 transforms to Na_2SO_4 (I) fast ion conduction hexagonal phase (α -phase) at about 240 °C. In the absence

of a detailed phase diagram, only a tentative interpretation can be given for the observed conductivity variation. According to the only available partial phase diagram of the binary system reported by Boeke⁹ in 1907 $\text{Na}_2\text{SO}_4(\text{I})$ based solid solution region extends from pure $\text{Na}_2\text{SO}_4(\text{I})$ at 250 °C to about 80 mol% Na_2WO_4 composition at 500 °C. A Na_2WO_4 based solid solubility region appears to extend from pure Na_2WO_4 to about 20 mol% Na_2SO_4 composition. Detailed phase structure at intermediated compositions are not given in this phase diagram.

Conductivity isotherms at different temperatures below 500 °C, depicted in Fig.3, clearly shows the existence of two conductivity maxima, one around 22 mol% Na_2WO_4 composition and the other around 42 mol% Na_2WO_4 composition. The first conductivity maximum corresponds to a $\text{Na}_2\text{SO}_4(\text{I})$ based solid solution. The maximum conductivity in the $\text{Na}_2\text{SO}_4(\text{I})$ based solid solution region at 22 mol% Na_2WO_4 composition has a value of $4.0 \times 10^{-4} \text{ Scm}^{-1}$ at 450 °C. This is a four fold increase compared to pure Na_2SO_4 at the same temperature. This conductivity enhancement resulting from homovalent anion substitution is less than the enhancement reported for $\text{Na}_2\text{SO}_4(\text{I})$ by cation substitution²⁻⁵. The observed conductivity enhancement in the $\text{Na}_2\text{SO}_4(\text{I})$ based solid solubility region appears to be associated with increasing defect concentration and with lowering of activation energy. WO_4^{2-} substitution, apparently gives rise to excess lattice expansion which facilitates the creation of defects and

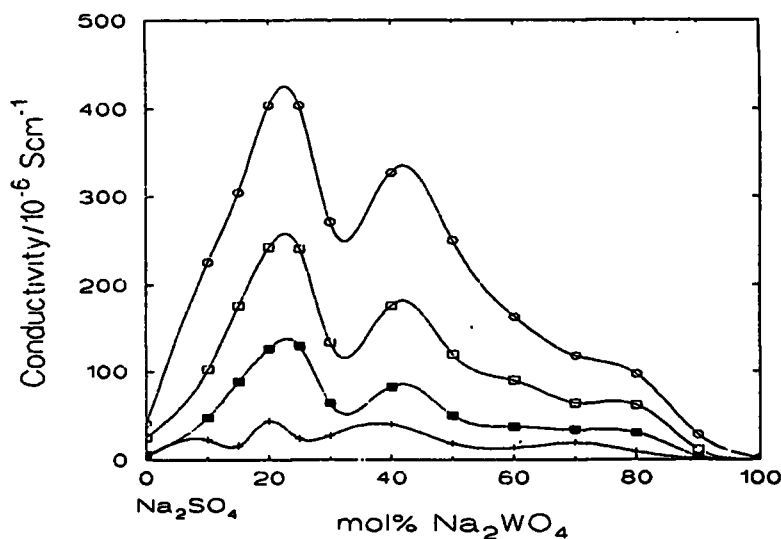


Fig.3. Variation of ionic conductivity with mol% Na_2WO_4 in Na_2SO_4 for four different temperatures. (+) 300°C. (■) 350 °C, (□) 400 °C, (○) 450 °C.

lowering the activation energy. This effect is optimized at 22 mol% Na_2WO_4 composition. Activation energies obtained from this study for pure $\text{Na}_2\text{SO}_4(\text{I})$ and for the maximum conductivity composition with 22 mol% are 0.74 eV and 0.5 eV respectively.

The available phase diagram shows a solid solution region based on Na_2WO_4 beyond 80 mol% Na_2WO_4 . Recent XRD analysis by Prakash et al⁷ have shown that the region from 30-60 mol% Na_2WO_4 corresponds to a two-phase mixture consisting of $\text{Na}_2\text{SO}_4(\text{I})$ based solid solution and Na_2WO_4 based solid solution. Conductivity enhancement observed by us in these compositions showing a maximum of $3.5 \times 10^{-4} \text{ Scm}^{-1}$ at 450 °C around 42 mol% Na_2SO_4 composition could possibly be due to the composite effect where the interfacial conductivity between grains contributes appreciably to the overall ionic conductivity. Similar enhancement has been reported by us for the two-phase binary mixtures $\text{Li}_2\text{SO}_4\text{-Li}_2\text{CO}_3$ ¹⁰, and $\text{Li}_2\text{SO}_4\text{-Li}_2\text{WO}_4$ ¹¹ and for several other composite systems.¹²

4. CONCLUSIONS

From the study of electrical conductivity of the $\text{Na}_2\text{SO}_4\text{-Na}_2\text{WO}_4$ binary systems, we conclude that in the $\text{Na}_2\text{SO}_4(\text{I})$ based solid solubility region, the conductivity increases as SO_4^{-2} ions are substituted by larger WO_4^{-2} ions in the crystal structure. The conductivity enhancement appears to be associated with lowering of the activation energy due to lattice expansion, facilitating cation migration. This effect is optimized at around 22 mol% Na_2WO_4 . The conductivity enhancement observed in the 30-60 mol% Na_2WO_4 composition region can be associated with the composite effect in the two-phase mixture consisting of $\text{Na}_2\text{SO}_4(\text{I})$ based and Na_2WO_4 based solid solutions.

ACKNOWLEDGEMENTS

Research support provided by the International Programs in the Physical Sciences (IPPS), Uppsala University, Sweden is acknowledged. We are thankful to Professor R. P. Gunawardane for helpful discussions.

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